

Translation from Japanese

19. Japanese Patent Office (JP)

11. Publication No. (Kokai): **6-16402**

12.

PATENT APPLICATION (A)

43. Date of publication of application: January 25, 1994

51. Int. Cl ⁵ ..	ID Code(s)	Intra-Bureau Nos.:	F I	Technical Classification
C01B 21/22				
B01D 53/04	Z			
B01J 23/34	M	8017-4G		
//B01D 53/14	A			

Request for Examination: Not yet submitted Number of Claims: 4 OL (Total of 4 pages [in original])

21. Application Number: 4-169110	71. Applicant: Japan Bionics Co., Ltd. 1-1-3 Nishishimbashi, Minato-ku, Tokyo
22. Date of filing: June 26, 1992	72. Inventor: Takashi Shimada c/o Nippon Bionics Hiratsuka Plant No. 5181 Tamura, Hiratsuka-shi, Kanagawa-ken
	72. Inventor: Keiichi Iwata c/o Nippon Bionics Hiratsuka Plant No. 5181 Tamura, Hiratsuka-shi, Kanagawa-ken
	72. Inventor: Masako Yasuda c/o Nippon Bionics Hiratsuka Plant No. 5181 Tamura, Hiratsuka-shi, Kanagawa-ken

54. [Title of the Invention]: **METHOD FOR PURIFYING NITROUS OXIDE**

57. [Abstract]:

[Object]

To obtain a high-purity purified gas by reliably removing oxygen contained as an impurity in nitrous oxide or in a gas containing nitrous oxide without creating as byproducts impurities such as nitrogen that are generated by the decomposition of nitrous oxide.

[Means for Solution]

Nitrous oxide or a gas containing nitrous oxide diluted with nitrogen, argon, etc., is brought into contact with a catalyst consisting essentially of manganese oxide, especially a low-grade manganese oxide. In addition, the catalyst is brought into contact with nitrous oxide, as required, prior to refinement and pretreated.

Claims

[Claim 1]

A method for purifying nitrous oxide, said method characterized by the fact that coarse nitrous oxide is brought into contact with a catalyst consisting essentially of manganese oxide, and the oxygen contained in said coarse nitrous oxide is removed.

[Claim 2]

A method for purifying according to claim 1, wherein the manganese oxide is 1, 2 or more compounds selected from among manganese monoxide (MnO), dimanganese trioxide (Mn_2O_3), or trimanganese tetroxide.

[Claim 3]

A method for purifying nitrous oxide according to claim 1, wherein prior to purification, pretreatment of the catalyst is performed by bringing the catalyst into contact with nitrous oxide at a temperature higher than the temperature at the time of purifying.

[Claim 4]

A purifying method according to claim 3, wherein the difference between the pretreatment temperature by nitrous oxide and the temperature at the time of purification is 10 to 100°C.

Detailed Description of the Invention

[0001]

[Industrial Field of Application]

The present invention relates to a purifying method for nitrous oxide, more specifically, a purification method for nitrous oxide that is able to remove oxygen contained as an impurity in nitrous oxide to extremely low concentrations. Nitrous oxide is used in semiconductor manufacturing, for example, in the formation of silicon oxidation films used for surface insulation films during LSI production, but as film manufacturing technology has advanced, so has the demand for extremely low impurity levels.

[0002]

[Prior Art]

Nitrous oxide that is used in semiconductor manufacturing is generally sold commercially in the form of a pure nitrous oxide (liquefied gas). Oxygen and moisture in particular are contained as impurities in these nitrous oxides, and of these the moisture can be removed by means of a dehydration agent such as synthetic zeolite. The oxygen concentration in commercially sold nitrous oxides is generally

20 ppm or less, but in high-purity nitrous oxides of approx. 5-9 contained in canisters, the oxygen concentration is comparatively low at 0.1 to 1 ppm.

[0003]

[Problems that the Invention is to Solve]

Nevertheless, if the oxygen content is a level which exceeds 1 ppm, if it cannot fully satisfy the demands in recent semiconductor manufacturing processes, and reduction to 0.1 ppm or less, preferably 0.01 ppm or less, has been strongly desired. Moreover, in recent years it has become possible to purify gases such as silane that is used at the same time as nitrous oxide gases in semiconductor manufacturing to high levels of purity, and those containing oxygen in the amount of 0.01 ppm or less as an impurity, for example, have been obtained (Kokai No. 3-12303, etc.). For this reason as well, the demand for extremely low oxygen content in nitrous oxide is increasing. Furthermore, since these nitrous oxides can be contaminated by the admixture of impurities such as air, in the process of being supplied to the semiconductor device, for example, when the canister comes in contact, or when the piping is switched, ultimately removing the impurities immediately before the device is desirable. Although such demands for high-purity nitrous oxide have been increasing from year to year, the constitution of the device is complex. A method of aeration in an alkaline aqueous solution of dithionite is known, as a method of removing oxygen contained in nitrous oxide, but since this is a wet method, it is not only disadvantageous from the standpoint of convenience, but an actual moisture removal (process) will become necessary. For this purpose, a method that can be used by filling a purifying tube with a deoxygenation catalyst as in the purification of nitrogen or inert gases is desired. However, with deoxygenation catalysts such as reduced nickel, the problem encountered is that the nitrous oxide almost completely decomposes at room temperature.

[0004]

[Means Used to Solve the Problems]

The present inventors, as the result of intensive studies concerning purification methods which are able to remove with high efficiency the oxygen contained in nitrous oxide down to extremely low concentrations without decomposing the nitrogen oxide, found that by bringing nitrous oxide into contact with the catalyst consisting essentially of a manganese oxide, oxygen can be removed to a level of 0.1 ppm or less, or even 0.01 ppm or less, and that the decomposition of the nitrous oxide is low, thus achieving the present invention. Specifically, the present invention is a purification method for nitrous oxide characterized by the fact that oxygen contained in coarse nitrogen oxide is removed by bringing said coarse nitrogen oxide into contact with a catalyst consisting mainly of manganese oxide.

The present invention can be used in the removal of oxygen contained in both nitrous oxide represented by the chemical formula N_2O alone or nitrous oxide that has been diluted (generally

referred to as coarse nitrogen oxide) with an inert gas (inert gas base) such as nitrogen or argon.

[0005]

Various types of manganese oxide can be used in the present invention, but a lower oxide of manganese is generally preferable. Lower oxides refer to manganese monoxide represented by the chemical formula MnO , dimanganese trioxide represented by Mn_2O_3 , trimanganese tetroxide represented by Mn_3O_4 , and mixtures thereof. Various methods can be used for obtaining these lower oxides. Nonetheless, a method of reducing a higher oxide such as manganese dioxide with hydrogen or carbon monoxide is representative, and depending upon the reduction conditions, lower oxides of various compositions such as the respective oxides separately or mixtures of 2 or more such oxides can be obtained. It is also possible to produce these oxides from manganese salts having the corresponding oxidation number, for example, in order to obtain manganese monoxide, there are methods such as heating manganese(II) carbonate, manganese(II) hydroxide, manganese(II) oxalate, manganese (II) acetate, etc., in an airtight state. These manganese oxides can be used in a molded form, as is or can be pulverized into a suitable size and used, or even used in a form which holds onto a catalyst carrier. As one method of attaching manganese oxide onto a carrier, a carrier powder such as diatomaceous earth, alumina, silica-alumina, aluminosilicate, or calcium silicate is dispersed in an aqueous solution of a manganese salt, and then allow the manganese constituent to settle on the carrier powder. Next, after the cake obtained by filtration and washing with water, as necessary, has been dried at 120 to 150°C, it is baked in nitrogen at 300°C or above. The baked product is pulverized. The product or other such methods as an inorganic salt of MnCO_3 , $\text{Mn}(\text{OH})_2$, etc., or an organic salt of MnC_2O_4 , or $\text{Mn}(\text{CH}_3\text{COO})_2$ are baked in nitrogen and then pulverized. A heat-resistant cement is blended with this, and it is again baked in nitrogen. These manganese oxides normally can be made into a molded body by extrusion molding, stamp molding, etc., and can be used as they are or after being pulverized into pieces of a suitable size as necessary. A dry method or wet method can be used as the molding method, and in this process small amounts of water, lubricant, etc., can be used. In the handling operation when a lower manganese oxide is used, the material must be handled so as not to come in contact with oxygen, for example, in a nitrogen gas atmosphere in a glove box. As the amount of manganese oxide contained, normally 10 wt % or more, preferably 20 wt % or more, should be contained mainly as lower oxides of manganese. When the amount of manganese oxide contained is less than 10 wt %, the deoxygenation capacity is lowered, and there is the risk that oxygen cannot be removed sufficiently.

[0006]

In the present invention, purification can be performed by filling the purification tube with a molded body having manganese oxide, preferably a lower oxide, as its active ingredient, and then allowing

the coarse nitrous oxide to pass through, but it is desirable to perform pretreatment by means of nitrous oxide prior to purification in order to prevent the decomposition of the nitrous oxide. Pretreatment is performed by passing nitrous oxide alone or a gas mixture with another inert gas such as argon for 30 min to 2 hrs. normally at a tube velocity (LV) of 1 to 10 cm/sec. Pretreatment is performed at a higher temperature than the temperature at the time of purification of the coarse nitrous oxide, normally 50°C or higher. However, if the temperature is too high, there is a risk of the deoxygenation activity as a catalyst being impaired by a reaction with the nitrous oxide. Due to this possibility it is desirable that it be performed in a temperature range that is 10 to 100°C higher than the temperature at the time of purification. When pretreatment is not performed, the concentration of nitrogen, produced by the decomposition of the nitrous oxide depending upon the conditions during purification, may reach close to 3 vol. %. However, by performing pretreatment, this admixture of nitrogen due to decomposition can be nearly completely eliminated with good reliability. Pretreatment may be performed before filling or after filling the purification tube, but if pretreatment is performed after the purification tube is first filled with manganese oxide, the purification of coarse nitrous oxide can be performed immediately thereafter, which is convenient.

[0007]

Purification of coarse nitrous oxide is performed by passing the coarse nitrous oxide through a purification tube that has been filled with the aforesaid catalyst consisting mainly of manganese oxide, and by bringing the coarse nitrous oxide into contact with the manganese oxide catalyst, the oxygen contained as an impurity can be removed without causing the decomposition of the nitrous oxide. The oxygen concentration in the coarse nitrous oxide suitable for use in the present invention is normally below 100 ppm. If the oxygen concentration becomes higher than this, the calorific value will increase, requiring a heat removal device depending upon the conditions.

[0008]

The filling length of the manganese oxide catalyst that is used to fill the purification tube is determined by the amount of coarse nitrous oxide supplied, the oxygen concentration, the characteristics of the catalyst used or the oxygen removal method and conditions, etc., but normally is 50 to 1500 mm. If the filling length becomes less than 50 mm, there is the risk of reduction in the oxygen removal ratio, and if it exceeds 1500 mm, there is a risk of increased pressure loss. Additionally, the tube velocity (LV) of the coarse nitrous oxide during purification, will vary according to the oxygen concentration in the coarse nitrous oxide supplied, operating conditions, etc., and cannot be stated categorically, but normally should be 100 cm/sec or less, preferably 30 cm/sec or less. The contact temperature of the nitrous oxide and manganese oxide catalyst has the temperature of the gas supplied to the inlet of the purification tube is normally 50°C or less, preferably 0 to 40°C. If the contact temperature is too high,

the nitrous oxide may break down, and not only will the deoxygenation capacity be impaired, but there is a risk that nitrogen will be generated as an impurity. As to the pressure of the gas during contact, treatment can be performed at normal pressure, depressurization, or compression, but normally the pressure should be no greater than 10 kg/cm² abs, preferably 0.1 kg to 5 kg/cm² abs. When the pressure is too high, there is the risk of decomposition of the nitrous oxide.

[0009]

In the present invention, there is no harmful effect in particular on the deoxygenation capacity even when small amounts of moisture are contained in the nitrous oxide, and also when a carrier, etc., is used, the moisture can be removed simultaneously depending upon the type of carrier used. Additionally, it is also possible to combine a suitable moisture removal process using a dehydration agent such as a synthetic zeolite as necessary in the oxygen removal process using manganese oxide. By this means it is possible to remove moisture completely and to obtain a purified nitrous oxide having an extremely high purity.

[0010]

[Working Examples]

Working Example 1

[Preparation of Purification Tube]

A commercially sold manganese oxide catalyst was used. This material was an extruded product of MnO₂ and was black in color. This was pulverized, sifted to 8 to 12 mesh, and 63 mL was used to fill a stainless steel purification tube having an internal diameter of 16.4 mm, a length of 400 mm, and a fill length of 300 mm (fill density 1.6 g/mL). After the interior of the system was purged while being preheated by flushing with nitrogen at a temperature of 300°C and a flow rate of 250 mL/min or 1 hr, reduction treatment was performed by passing carbon monoxide through the tube for 3 hrs at a flow rate of 127 mL/min (LV = 1 cm/sec). Next, switching to nitrogen, the system was cooled to room temperature. Additionally, as a result of reduction under the same conditions in a quartz tube, the color of the catalyst changed to green, confirming that the MnO₂ was reduced and a lower oxide of manganese had been produced.

[Purification of Coarse Nitrous Oxide]

Without interruption purification was performed using the aforesaid stainless steel purification tube. 50% nitrous oxide (helium base), containing 0.8 ppm oxygen as an impurity, was passed through the purification tube at 1266 mL/min (LV = 10 cm/sec), and when the oxidation concentration in the outlet gas was measured using a yellow phosphorous light emission type oxygen analyzer (measurement lower limit concentration 0.01 ppm), oxygen was not detected and was less than 0.01 ppm.

Additionally, when the nitrogen concentration in the outlet gas was measured by means of a gas chromatograph (detector TCD), it was found to be 1.3%. At 100 min following the beginning of purification, the oxygen concentration in the outlet gas was less than 0.01 ppm, and the nitrogen concentration became 0.55%.

[0011]

Working Example 2

[Preparation of Purification Tube]

A purification tube was prepared under the same conditions as in Working Example 1. Prior to purification of the nitrous oxide, the purification tube was heated to 100°C, and pretreatment was performed by passing a 50% nitrous oxide (helium based) through it at normal pressure at 127 mL/min (LV = 1 cm/sec) for 30 min.

[Purification of Nitrous Oxide]

In the same way as in Working Example 1, 50% nitrous oxide (helium based) containing 0.8 ppm of oxygen as an impurity was passed through this purification tube at 1266 mL/min (LV = 10 cm/sec), and when the outlet gas was analyzed, the oxygen concentration was found to be less than 0.01 ppm and the nitrogen concentration 230 ppm. The oxygen concentration in the outlet gas 100 min after purification was started was less than 0.01 ppm, and the nitrogen concentration was 170 ppm.

[0012]

Working Example 3

[Preparation of Purification Tube]

After a stainless steel purification tube was filled with a commercially sold manganese catalyst in the same way as in Working Example 1, reduction treatment was performed by passing hydrogen through the tube at 200°C at a flow rate of 127 mL/min (LV = 1 cm/sec) under normal pressure for 4 hrs. When reduction was performed under the same conditions in a quartz tube separate from this example, it was confirmed that the color of the catalyst changed to a gray-brown. Also, when the catalyst in the quartz tube was taken out into the air and identification was performed immediately by means of a powder X-ray diffraction device, it was confirmed to be a blended manganese oxide composed mainly of manganese monoxide and dimanganese trioxide.

[Purification of Nitrous Oxide]

When 50% nitrous oxide (helium base) containing 0.8 ppm oxygen was passed through this purification tube in the same way as in Working Example 1 and the outlet gas was analyzed, the oxygen concentration was less than 0.01 ppm and the nitrogen concentration was 360 ppm. The

oxygen concentration in the outlet gas 100 min after the beginning of purification was less than 0.01 ppm and the nitrogen concentration was 180 ppm.

[0013]

Comparative Example 1

[Preparation of Purification Tube]

A commercially sold nickel catalyst (N-111, manufactured by Nikki K.K.) was used. The composition of this material was in the form of Ni + NiO, with 45 to 47 wt % as Ni, 2 to 3 wt % Cr, 2 to 3 wt % Cu, 27 to 29 wt % diatomaceous earth, and 4 to 5 wt % graphite, and was a molded body having a diameter of 5 mm and a height of 4.5 mm. 63 mL of this nickel catalyst pulverized to a granulation of 8 to 10 mesh, was used to fill a purification tube similar to that used in the working examples (fill density 1.0 g/mL). After this was subjected to reduction treatment for 3 hrs with hydrogen at normal pressure, a temperature of 150°C, and a flow rate of 595 mL/min (LV = 3.6 cm/sec), it was cooled to room temperature.

[Purification of Nitrous Oxide]

When coarse nitrous oxide was passed through this purification tube in the same way as in Working Example 1, the purification tube generated excessive heat. When the outlet gas was analyzed at this point, the oxygen concentration was less than 0.01 ppm, but nitrous oxide could not be detected, with only nitrogen detected, indicating that nearly all of the nitrous oxide had decomposed.

[0014]

[Effects of the Invention]

In the present invention, it is possible to remove oxygen in nitrous oxide which has been difficult to remove in the past to a low concentration of less than 0.1 ppm or even less than 0.01 ppm, the admixture of impure elements due to the decomposition of the nitrous oxide during purification can be prevented, and a high-purity nitrous oxide can be obtained.